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Application of  
Applicant(s) : A. Faur-Ghenciu  
Serial No. : 10/617,146  
Filed : July 10, 2003  
Title : HIGH ACTIVITY WATER GAS SHIFT CATALYSTS  
BASED ON PLATINUM GROUP METALS AND  
CERIUM-CONTAINING OXIDES  
Docket No. : GMC 0025 PA / 42320.29/GP-3  
Examiner : K. Handal  
Art Unit : 1764

Assistant Commissioner for Patents  
Washington, D.C. 20231

Sir:

CERTIFICATE OF FACSIMILE TRANSMISSION  
I hereby certify that this paper is being facsimile transmitted to  
the Patent and Trademark Office (Fax No. 571/273-8300) on  
December 20, 2006.

*Patricia L. Prior*  
Patricia L. Prior, Attorney Reg No. 33,758

**DECLARATION OF ANCA FAUR-GHENCIU, NATHAN E. TRUSTY,  
MARK R. FEAVIOUR, JESSICA G. REINKINGH, PHILLIP SHADY, AND  
PAUL J. ANDERSEN UNDER 37 C.F.R. 1.131**

Anca Faur-Ghenciu, Nathan E. Trusty, Mark R. Feaviour, Jessica G. Reinkingh, Phillip Shady, and Paul J. Andersen, the applicants in the above-identified patent application, declare as follows:

1. We are the inventors of claims 1-61 of the above-identified patent application and inventors of the subject matter described and claimed therein.
2. Prior to March 28, 2002, we reduced the present invention to practice as evidenced by Exhibits A-C attached hereto.
3. Exhibit A is a copy of a Record of Invention prepared with respect to the present invention. The Record of Invention includes a brief description of the invention, testing conditions, various catalyst formulations, results and conclusions, and references to supporting data.

Serial No. 10/617,146  
Docket No. GMC 0025 PA/40320.29/GP-3

4. Exhibit B is a copy of pages 17-30 of Laboratory Notebook No. 1875. These pages show the preparation of several catalysts of the present invention as well as comparison examples. Pages 23, 25, and 29 are referred to on page 4 of the Record of Invention.

5. Exhibit C is a copy of an email from Peter Gray of Johnson Matthey PLC to James Saller of General Motors Corporation, the assignee of the present invention, with an attachment forwarding the Record of Invention for the present invention.

6. Each of the dates deleted from Exhibits A-C is prior to March 28, 2002. All work relating to the conception and reduction to practice of this invention was carried out in a WTO country.

The declarants further state that the above statements were made with the knowledge that willful false statements and the like are punishable by fine and/or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of this application or any patent resulting therefrom.

Date: \_\_\_\_\_

See attached sheet  
Anca Faur-Ghenciu

Date: \_\_\_\_\_

See attached sheet  
Nathan E. Trusty

Date: \_\_\_\_\_

See attached sheet  
Mark. R. Feaviour

Date: \_\_\_\_\_

See attached sheet  
Jessica G. Reinkingh

Serial No. 10/617,146  
Docket No. GMC 0025 PA/40320.29/GP-3

Date: \_\_\_\_\_

See attached sheet  
Phillip Shady

Date: \_\_\_\_\_

See attached sheet  
Paul J. Andersen

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Date: Dec 14, 2006

Anca Faur-Ghenciu  
Anca Faur-Ghenciu

Date: \_\_\_\_\_

\_\_\_\_\_  
Nathan E. Trusty

Date: \_\_\_\_\_

\_\_\_\_\_  
Mark. R. Feaviour

Date: \_\_\_\_\_

\_\_\_\_\_  
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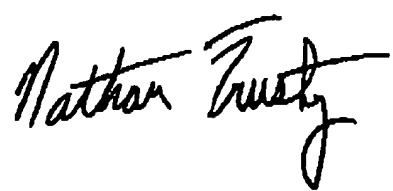
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Date: \_\_\_\_\_

Anca Faur-Ghenciu

Date: 12/13/06

Nathan E. Trusty



Date: \_\_\_\_\_

Mark. R. Feavlor

Date: \_\_\_\_\_

Serial No. 10/617146

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Date: \_\_\_\_\_

\_\_\_\_\_  
Anca Faur-Ghenciu

Date: \_\_\_\_\_

\_\_\_\_\_  
Nathan E. Trusty

Date: 13<sup>th</sup> Dec 2006

M. Faur  
Mark R. Faur

Date: \_\_\_\_\_

\_\_\_\_\_  
Jessica G. Reinkingh

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\_\_\_\_\_  
Anca Faur-Ghenciu

Date: \_\_\_\_\_

\_\_\_\_\_  
Nathan E. Trusty

Date: 12/13/2007

\_\_\_\_\_  
Mark R. Feaviour

Date: \_\_\_\_\_

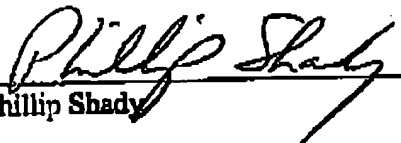
\_\_\_\_\_  
Jessica G. Reinkingh

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Date: 12/13/2006

Date: \_\_\_\_\_

  
Phillip Shady

\_\_\_\_\_  
Paul J. Andersen



Serial No. 10/617146

Docket No. GMC 0025 PA/40320.29/GP-3

Date: \_\_\_\_\_

Date: December 13, 2006

\_\_\_\_\_  
Phillip Shady

Paul J. Andersen  
Paul J. Andersen



**Johnson Matthey Fuel Cells**  
*the power within*

Exhibit "A"

**RECORD OF INVENTION**

**Title of Invention:** High Activity Water Gas Shift Catalysts Based on Promoted Platinum Group Metals - Ceria-containing Oxides

**Record Written by:** Anca Ghenciu

**Date Record Written:**

**Brief Description of Invention:**

In the catalyzed water gas shift (WGS) reaction, the high activity WGS catalyst systems consisting of 1-4% platinum, or palladium, or platinum-palladium, or platinum-iridium, dispersed on or in the lattice of ceria-zirconia or ceria-lanthana mixed oxides with various ratios ceria-zirconia or ceria-lanthana, respectively, said catalysts including a 0.1%-1% promoter comprising of one or more alkali or alkaline-earth metals selected from the group of cesium, lithium, rubidium, potassium, or magnesium, strontium, barium, said catalyst including support dopants such as lanthanum, praseodymium, neodymium, all said catalysts tested in the presence of carbon monoxide, water, carbon dioxide and hydrogen, with best catalytic performance between 200°-400°C, preferably 250°-375°C. The invention also relates to the use of said catalysts as coated on monolithic supports for the WGS reaction.

Catalyst testing: fixed bed reactor, 1 g catalyst and 1 g cordierite 45-60 mesh, under the following reaction conditions: 8%CO, 30%H<sub>2</sub>O, 10%CO<sub>2</sub>, 32.5%H<sub>2</sub>, 1%CH<sub>4</sub>, balance N<sub>2</sub>, in a fixed bed reaction system, at 67,500 cc/g cat /hr weight hourly space velocity, between ~150° and ~600°C. Test results in each case (Examples) to be written.

**Results and conclusions:**

1. The ceria-zirconia mixed oxides show improved catalytic performance over ceria-lanthana, also over ceria- or zirconia-only. The ceria-zirconia catalysts of this invention show a decrease in the onset temperature of the WGS reaction (light-off temperature). Possible reasons for the improved catalytic activity conferred by ceria-zirconia mixed oxides:

- High thermal stability therefore improved durability/long-term stability conferred by the mixed oxide phase.
- Improved water adsorption properties compared to ceria-only supports (here citation of previously known 1%Pt/CeO<sub>2</sub> catalyst), yet while keeping the oxygen mobility as conferred by ceria.
- Higher metal dispersion on ceria-zirconia mixed oxides than on ceria when the same method of metal deposition is used.
- Optimum ceria: zirconia ratio for the oxides studied ~ 20:80. Advantage of high Zr:Ce ratio perhaps due to improved water adsorption properties, that may also reflect in a better durability. A ceria content is necessary, since Pt/zirconia has poorer performance.

2. All platinum-ceria-zirconia mixed oxides of this invention show better activity than palladium,

platinum-palladium, or platinum-iridium catalysts in combination with the same oxides and prepared in the same manner. Platinum formulations offer advantage over palladium formulations based on the temperature difference between the onset of WGS and the onset of methanation; the no-methanation window for WGS reaction is wider in the case of Pt catalysts than for Pd formulations.

3. For the unpromoted formulations, methane formation is seen to a small extent at temperatures higher than 350°C under the testing conditions. The alkali and alkaline-earth promoters reduce the extent of methanation (conversion to methane formation) and/or shift the onset of methanation to higher temperatures.

#### 4. Role of alkali and alkaline-earth promoters

- Improve the water adsorption/chemisorption properties of the oxidic support (also known from the technical literature as promoters for several partial oxidations and epoxidations). A more pronounced increase in the catalytic activity is seen in the case of Ce-rich mixed oxides than in the case of Zr-rich or La-rich ceria-containing mixed oxides.
- Reduce the extent of methanation. The temperature corresponding to the onset of methanation is higher in the case of Li than in the case of Cs (see "3" above).
- An improvement consisting of more than 50°C decrease in the temperature corresponding to the maximum catalytic activity is obtained with Cs- or Li/2%Pt/CeO<sub>2</sub>-ZrO<sub>2</sub> (58:42 wt%) compared to the unpromoted formulation, 2%Pt/CeO<sub>2</sub>-ZrO<sub>2</sub> (58:42 wt) or the known to the art Pt/CeO<sub>2</sub>.

5. Pt/Zr-rich ceria-zirconia formulations, even when unpromoted with alkali, show the same high activity as the alkali-promoted Pt/stoichiometric oxide, possibly due to improved water chemisorption with the increase in Zr content. The difference between the two may consist in long-term performance and durability.

#### 6. Role of chosen dopants

- La, Pr, Nd improve the thermal stability of the support. Some reduction in activity seen in some cases.

Perhaps to also cover (or publication):

Impact of catalyst preparation method and material properties on catalyst performance, role of the metal-oxide interface in the catalytic activity: Pt-O-CeO<sub>x</sub>-ZrO<sub>x</sub>, continuum phase.

#### Novelty of the Invention:

Under the reaction conditions chosen for testing: 1. Very high activity catalysts comprised of Pt, Pt-Pd, Pt-Ir/ceria-zirconia mixed oxides with different CeO<sub>2</sub>:ZrO<sub>2</sub> ratios for medium temperature range WGS reaction, 200-400°C, preferably 300°-375°C. 2. 1-4%Pt supported on ceria-zirconia mixed oxides show higher WGS activity than the similarly prepared Pt catalysts supported on either ceria-only or on zirconia-only, for the same Pt content. 3. For Pt/ceria-zirconia catalysts, a Zr-rich formulation (i.e., CeO<sub>2</sub>-ZrO<sub>2</sub> 20:80, wt%) shows higher WGS activity than the stoichiometric oxide (CeO<sub>2</sub>:ZrO<sub>2</sub> 58:42, wt%) and also than a Ce-rich oxide (i.e., CeO<sub>2</sub>:ZrO<sub>2</sub> 70:30, wt%), but also than the Zr-only formulations. 4. Cesium and Lithium promotion of the Pt/ceria-zirconia catalysts leads to further improvement in the WGS activity, at temperatures lower than in the case of the unpromoted catalysts. Over 50°C decrease in the temperature corresponding to the maximum catalytic activity is obtained with Cs- or Li/2%Pt/CeO<sub>2</sub>-ZrO<sub>2</sub> (58:42

wt%) compared to the unpromoted formulation, 2%Pt/CeO<sub>2</sub>-ZrO<sub>2</sub> (58:42 wt) or the known to the art Pt/CeO<sub>2</sub>. 5. The effect of promoters in the increase in activity is more pronounced in the case of Ce-rich formulations than for the Zr-rich formulation. 6. The ceria-zirconia ratio is estimated to play a role in durability. 7. For all CeO<sub>2</sub>-ZrO<sub>2</sub> formulations studied, the alkaline metal promotion contributes to the reduction in methane formation. 8. Promotion with Li shifts the onset of methanation to slightly higher temperatures than the promotion with Cs.

#### Benefit of Invention:

1. Catalyst formulations with very high catalytic activity for WGS reaction at medium temperature (300°-375°C), for the production of hydrogen. High catalytic activity with no methane formation below 350°C and minimum methane formation at temperatures higher than 350°C, in the presence of Pt/ceria-zirconia or Pt/ceria-lanthana mixed oxides, and thier alkali- or alkaline-earth promoted formulations. 2. Improved catalytic activity with Cs- and Li-promoted Pt dispersed on/in CeO<sub>2</sub>-ZrO<sub>2</sub> mixed oxides, at lower temperatures and with higher activity and selectivity than for Pt dispersed on CeO<sub>2</sub> or ZrO<sub>2</sub> only. 3. Improved catalytic activity for WGS with high Zr/Ce ratios. 4. Reduction in the methanation activity obtained in the presence of alkali-promoted formulations. 5. Thermally stable catalytic materials based on the high thermal stability of the Ce-Zr mixed oxides. 6. Possible improved thermal durability through the use of support dopants: Nd, Pr, La.

#### References to Supporting Work (e.g. Lab Notebook Number):

|               |   |
|---------------|---|
| 1757-86-243   | 1%Pd/[90(CeO <sub>2</sub> -ZrO <sub>2</sub> 20:80)-10(Al <sub>2</sub> O <sub>3</sub> )]               |
| 1757-113-243C | 1%Pd/[90(CeO <sub>2</sub> -ZrO <sub>2</sub> 20:80)-10(Al <sub>2</sub> O <sub>3</sub> )]               |
| 1757-93-253   | 1%Pd/[80(La <sub>2</sub> O <sub>3</sub> -CeO <sub>2</sub> 60:20)-20(Al <sub>2</sub> O <sub>3</sub> )] |
| 1757-131-1    | 1%Pd/75%La <sub>2</sub> O <sub>3</sub> -25%CeO <sub>2</sub>   |
| 1757-131A2    | (1%Pd-0.5%Pt)/75%La <sub>2</sub> O <sub>3</sub> -25%CeO <sub>2</sub>                                  |
| 1757-133-4    | (1%Pt-0.5%Cs)/75%La <sub>2</sub> O <sub>3</sub> -25%CeO <sub>2</sub>                                  |
| 1757-139-2    | 1%Pt/75%La <sub>2</sub> O <sub>3</sub> -25%CeO <sub>2</sub>   |
| 1757-136-1    | 1%Pd/25%La <sub>2</sub> O <sub>3</sub> -75%CeO <sub>2</sub>   |
| 1757-137-2    | (1%Pd-0.5%Pt)/ 25%La <sub>2</sub> O <sub>3</sub> -75%CeO <sub>2</sub>                                 |
| 1757-141-1    | (1%Pt-0.5%Cs)/ 25%La <sub>2</sub> O <sub>3</sub> -75%CeO <sub>2</sub>                                 |
| 1757-140-1    | 1%Pt/ 25%La <sub>2</sub> O <sub>3</sub> -75%CeO <sub>2</sub>  |
| 1757-143-14   | (1%Pt-0.5%Cs)/CeO <sub>2</sub>  |
| 1757-161A     | 0.2%Cs/2%Pt/CeO <sub>2</sub> -  |
| 1875-009      | 0.2%CsHPA/2%Pt/CeO <sub>2</sub>   |
| 1757-164B     | 0.2%Ir/2%Pt/CeO <sub>2</sub> -.   |

|           |  |
|-----------|--|
| 1757-159B | 2%Pt/LaOx-CeO2 -   |
| 1875-010  | 0.2%CsHPA/2%Pt/LaOx-CeO2   |
| 1757-160B | 0.2%Cs/2%Pt/La-CeO2 -  |
| 1757-161B | 2%Pt/CeO2-ZrO2 (58:42 wt) -                                      |
| 1757-168A | 2%Pt/CeO2-ZrO2 (19.6 : 80.4 wt) -                                |
| 1757-186  | 0.2%Cs/2%Pt/CeO2-ZrO2 (19.6 : 80.4 wt) -                         |
| 1757-163B | 0.2%Cs/2%Pt/ CeO2-ZrO2 (58:42 wt) -                              |
| 1757-166B | (2%Pt-0.2%Cs)/CeO2-ZrO2 (58:42 wt) (c) -                         |
| 1757-167B | 0.2%Cs/2%Pt/ CeO2-ZrO2 (58:42 wt) (cc) -                         |
| 1757-168B | 2%Pt/CeO2-ZrO2 (70.5 : 29.5 wt) -                                |
| 1757-167A | 2%Pt/CeO2-ZrO2-La2O3 (54.4 : 40.6 : 3.8 wt) -                    |
| 1757-173A | repeat of 1757-166B -  |
| 1757-173B | (2%Pt-0.2%Cs)/CeO2-ZrO2 (58:42 wt) -                             |
| 1757-166A | 2%Pt/ CeO2-ZrO2 (58:42 wt) (c) - to be compared with 1757-161B - |
| 1757-177  | 2%Pt/0.2%Cs/CeO2-ZrO2 (58:42 wt) -                               |
| 1757-175  | 2%Pt/0.2%Cs/CeO2-ZrO2 (58:42 wt) (c) -                           |
| 1757-179  | same as 1757-163B -  |
| 1757-181A | 2%Pt/CeO2-ZrO2-La2O3-Nd2O3 (20 : 73.5 : 1.5 : 5 wt) -            |
| 1757-181B | 2%Pt/CeO2-ZrO2-La2O3-Nd2O3 (20 : 73.5 : 1.5 : 5 wt) (c) -        |
| 1757-188B | 2%Pt/(c) CeO2-ZrO2 (58:42 wt) -                                  |
| 1757-188A | 2%Pt/CeO2-FeOx -   |
| 1757-189A | 2%Pt/CeO2-ZrO2 (58 : 42 wt) (tp) -                               |
| 1757-189B | 2%Pt/CeO2-ZrO2 (19.6 : 80.4 wt) (tp) -                           |
| 1757-193B | repeat of 1757-188B -  |
| 1875-023  | xPt/CeOx-ZrOx -  |
| 1875-025  | ZrO2 - - Pt-CeOx   |
| 1875-029  | 2%Pt-ZrO2 -- CeO2 (42:58) -                                      |
| 1757-207A | 2%Pt/ZrO2 - July 01, 2001  |
| 1757-207B | 0.2%Cs/2%Pt/(c) CeO2-ZrO2 (58:42 wt) -                           |

|          |  |
|----------|--|
| 1944-005 | 0.1%Cs/2%Pt/CeO <sub>2</sub> -ZrO <sub>2</sub> (58 : 42 wt)  |
| 1944-007 | 0.5%Cs/2%Pt/CeO <sub>2</sub> -ZrO <sub>2</sub> (58 : 42 wt)  |
| 1944-009 | 1%Cs/2%Pt/CeO <sub>2</sub> -ZrO <sub>2</sub> (58 : 42 wt)    |
| 1944-013 | 1%Li/2%Pt/CeO <sub>2</sub> -ZrO <sub>2</sub> (58 : 42 wt)    |
| 1944-015 | 0.5%Li/2%Pt/CeO <sub>2</sub> -ZrO <sub>2</sub> (58 : 42 wt)  |
| 1944-065 | 1%Pt/2%Li/CeO <sub>2</sub> -ZrO <sub>2</sub> (58 : 42 wt)    |
| 1944-067 | 0.2%Li/2%Pt/CeO <sub>2</sub> -ZrO <sub>2</sub> (58 : 42 wt)  |
| 1944-069 | 5%Li/1%Pt/CeO <sub>2</sub> -ZrO <sub>2</sub> (58 : 42 wt)    |
| 1944-073 | 1%Li/1%Pt/CeO <sub>2</sub> -ZrO <sub>2</sub> (58 : 42 wt)    |
| 1944-075 | 2%Li/1%Pt/CeO <sub>2</sub> -ZrO <sub>2</sub> (58 : 42 wt)    |
| 1944-051 | 0.2%Ba/2%Pt/CeO <sub>2</sub> -ZrO <sub>2</sub> (58:42 wt) –  |
| 1944-053 | 0.2%K/2%Pt/CeO <sub>2</sub> -ZrO <sub>2</sub> (58:42 wt) –   |
| 1944-055 | 0.2%Sr/2%Pt/CeO <sub>2</sub> -ZrO <sub>2</sub> (58:42 wt) –  |
| 1944-049 | 0.2%Y/2%Pt/CeO <sub>2</sub> -ZrO <sub>2</sub> (58 : 42 wt) – |

**Contributors to the Invention:** A. Ghenciu, N. Trusty, M. Feaviour, J Reinkingh, P. Shady, P. Anderson

**If Invention has been discussed with or disclosed to external third parties, give details:**

Discussed with GM

**Witness Statement:**

***"On the date beside my signature, I read and understood the above invention"***

**Name:**

**Signature:**

**Date:**

TITLE

A. G.

PROJECT NO.

BOOK NO.

17

EXHIBIT "B"

File Name: 1875\_017 (1.6%Pt-CeO<sub>2</sub> TPC copp NaOH)  
Catalyst prep: N. Trusty/ A. Ghenciu

## Objective

WGS Catalyst: Prepare 1.6%Pt-CeO<sub>2</sub> by coprecipitation, using TPC and Ce(III) nitrate, % metal is by weight.

MATERIALS  
(shows actual weights used)

Tetramino-Platinum Chloride (TPC), JM stock solution, Lot # 689-691730-01B, 119.58 g Pt / l sol (105.40 g Pt / kg sol, d = 1.1345 g/ml) ..... 1.9 g  
Ce(NO<sub>3</sub>)<sub>3</sub> stock solution, JM, 395 g Ce/l, d=1.7 g/ml ..... 42.95 g (~25.3 ml)  
NaOH pellets ..... 9.1 g  
Deionized (DI) water (not including the water for washing the precipitate) ..... 1.175 l

## Calculation:

Calculated for 12.5 g 1.6%Pt/CeO<sub>2</sub> final material, containing:  
12.3 g CeO<sub>2</sub> and 0.2 g Pt

1. TPC solution needed for 0.2 g Pt:  
 $0.2 \times 1000 / 105.40 = 1.8975$  g TPC solution

2. Ce (III) nitrate solution needed for 12.3 CeO<sub>2</sub> in the final material:

moles CeO<sub>2</sub> =  $12.3 / 172.12 = 0.071462$  = moles Ce

amount Ce =  $0.071462 \times 140.12 = 10.0132$  g

Ce(III) solution =  $7.978 \times 1000 / 395 = 25.35$  ml Ce solution, or  $25.35 \times 1.7 = 43.095$  g Ce solution

3. NaOH solution needed, 5% excess:

3 moles / 1 mol Ce (III) solution, 2 moles / 1 mol Pt solution

$3 \times 0.071462 = 0.2144$  moles NaOH for Ce

$2 \times (0.2 / 195.09) = 0.00205$  moles NaOH for Pt

Total moles NaOH = 0.21644 moles; with 5% excess, 0.22726 moles NaOH

\*NaOH needed:  $0.22726 \times 40 = 9.1$  g

## Procedure:

The weighed amount of TPC and Ce(III) solutions were brought to 100 ml volume with DI water in an Erlenmeyer flask. The weighed amount of NaOH was dissolved into 1.1 liter DI water (~0.2N solution) and transferred to the reactor.

The coprecipitation was conducted at 90°C in a 3-liter glass reactor having a heating/cooling mantle, under vigorous stirring, by dosing the Pt and Ce solution during ca. 1 hr, subsurface. The pump dial was set at "Other," display 0.5 in the beginning followed by 2.5-2.7. During the precipitation, the color changed from light purple (in the beginning) to light yellow - white. The final pH was 8 (pH paper). After the addition of the precursor solution was complete, the precipitate was cured under stirring for ca. 1 hr at 90°C.

The precipitate was filtered and washed repeatedly with a total of 4.6 liter hot DI water (~55-60°C) to filtrate pH 6. The washing step included stirring (redispersing) the precipitate into hot water (85-90°C) with stirring, followed by filtration. The conductivity of the filtrate was not measured.

After filtration, the material was placed in a crucible and dried overnight (~15 hr) at ~125°C in an oven, static air. The dried material was calcined the second day in static air at 500°C for 2 hr. The catalyst was stored in a vial and labeled 1875-017. For WGS testing, the powder was pressed to 15 tons and sieved to 45-60 mesh.

The color change from purple to white during the precipitation should be further investigated. It may depend on the Pt precursor, or it may have been due to impurities in the reaction vessel.

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**Results &  
Analytical**After drying overnight, 6.12 g material was recovered  
calcination.

). No weight loss was recorded after

| Pt% | Ce% | Ce(III)/<br>Ce(IV) | SA,<br>m <sup>2</sup> /g | Pore<br>Volume,<br>cc/g | Pore Size<br>Distribution | SEM | TEM | XRD | TPR/<br>TPO | Pulse<br>Chemi-<br>sorption | ITK | Other |
|-----|-----|--------------------|--------------------------|-------------------------|---------------------------|-----|-----|-----|-------------|-----------------------------|-----|-------|
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A.G.



TITLE

PROJECT NO.

19

BOOK NO.

A.G.

File Name: 1875\_019 (2%Pt-CeO<sub>2</sub>-ZrO<sub>2</sub> 58:42 copp NaOH)

Tested as 1875-A

Catalyst prep: A Ghenciu/ N. Trusty

## Objective

WGS Catalyst: Prepare 2%Pt-CeO<sub>2</sub>-ZrO<sub>2</sub> (CeO<sub>2</sub>:ZrO<sub>2</sub> = 58:42, wt%) by coprecipitation, using nitrate precursors; % metal is by weight.MATERIALS  
(shows actual  
weights used)

Pt nitrate solution, JM, 233.42 g Pt/l sol. 149.33 g Pt/ kg sol, d = 1.5631 g/ml .....2.70 g  
 Ce(NO<sub>3</sub>)<sub>3</sub> stock solution, JM, 395 g Ce/l, d=1.7 g/ml .....40.0 g (~23.5 ml)  
 ZrO(NO<sub>3</sub>)<sub>2</sub> stock solution, JM, 203 g/l, d = 1.433 g/ml .....44 g (30.7 ml)  
 NaOH pellets.....15.0 g  
 Deionized (DI) water (not including the water for washing the precipitate) .....~1000 ml

## Calculation

Calculated for 20 g 2%Pt-CeO<sub>2</sub> final material, containing:19.6 g CeO<sub>2</sub>-ZrO<sub>2</sub> and 0.4 g Pt

1. Pt nitrate solution needed for 0.4 g Pt:  
 $0.4 * 1000 / 149.33 = 2.6786$  g Pt solution (1.7137 ml)
2. Ce (III) nitrate solution needed:  
 for 58% CeO<sub>2</sub>, 11.368 g CeO<sub>2</sub> in the final material  
 $\text{moles CeO}_2 = 11.368 / 172.12 = 0.066047 = \text{moles Ce}$   
 $\text{amount Ce} = 0.066047 * 140.12 = 9.2545$  g  
 $\text{Ce(III) solution} = 9.2545 * 1000 / 395 = 23.4291$  ml Ce solution, or  $23.4291 * 1.7 = 39.8295$  g Ce solution
3. ZrO<sup>2+</sup> solution needed:  
 for 42% ZrO<sub>2</sub>, 8.232 g ZrO<sub>2</sub> in the final material  
 $\text{moles ZrO}_2 = 8.232 / 123.224 = 0.066805 = \text{moles Zr}$   
 $\text{amount Zr} = 0.066805 * 91.224 = 6.09423$  g  
 $\text{ZrO}^{2+} \text{ solution} = 6.09423 * 1000 / 203 = 30.0209$  ml ZrO<sup>2+</sup> solution, or  $30.0209 * 1.433 = 43.0199$  g ZrO<sup>2+</sup> solution
4. NaOH solution needed, 10% excess:  
 3 moles/ 1 mol Ce (III) solution, 2 moles/ 1 mol ZrO<sup>2+</sup> solution, 2 moles/ 1 mol Pt solution  
 $3 * 0.066047 = 0.19814$  moles NaOH for Ce(III)  
 $2 * 0.066807 = 0.13361$  moles NaOH for ZrO<sup>2+</sup>  
 $2 * (0.4 / 195.09) = 0.004101$  moles NaOH for Pt  
 Total moles NaOH = 0.33585 moles; with 10% excess, 0.36943 moles NaOH  
 NaOH needed:  $0.36943 * 40 = 14.78$  g

## Preparation

The weighed amounts of Pt solution, Ce(III) solution, and zirconyl solution were mixed in an Erlenmeyer flask. The weighed amount of NaOH was brought to a 1-liter solution with DI water, in a volumetric flask (0.375N NaOH solution obtained), then transferred to the reactor.

The coprecipitation was conducted at 90-95°C in a 1.5-liter glass reactor having a heating/cooling mantle, under vigorous stirring, by dosing the Pt - Ce - Zr nitrate solution during 25 min, subsurface. The pump dial was set at "Other," display 0.5 in the beginning, then at 2.0. During the entire course of reaction, the color of the precipitate was light yellow-beige. The initial pH (NaOH solution) was 12.5-13 (pH paper). The final pH was not measured. After the addition of the precursor solution was complete, the precipitate was cured under stirring for ca. 1 hr at 90°C, then let stand overnight.

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Second day, the precipitate was filtered and washed repeatedly with a total of ~ 6 liter hot DI water (~55-60°C) to filtrate pH 6. The washing step included slurring (redispersing) the precipitate into hot water (85-90°C) with stirring, followed by filtration. Conductivity of the filtrate was not measured.

After filtration, the material was placed in a crucible and dried overnight (~15 hr) at ~125°C in an oven, static air. The dried material was calcined the second day in static air at 500°C for 2 hr. The catalyst was stored in a vial and labeled 1875-019 (1875-019A). For WGS testing, the powder was pressed to 15 tons and sieved to 45-60 mesh.

**Observations:****Results:****Analytical:**

| Pt % | Ce % | Ce(III)/Ce(IV) | Zr % | SA, m <sup>2</sup> /g | Pore Volume, cc/g | Pore Size Distribution | SEM | TEM | XRD | TPR/TPO | Pulse Chemisorption | ITK | Other |
|------|------|----------------|------|-----------------------|-------------------|------------------------|-----|-----|-----|---------|---------------------|-----|-------|
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TITLE

PROJECT NO.

21

BOOK NO.

A.G.

File Name: 1875\_021 (3%Pt-CeO<sub>2</sub>-ZrO<sub>2</sub> 56-44 copp NaOH)

Tested as 1875-B

Catalyst prep: A. Ghenciu/ N. Truisty

## Objective

WGS Catalyst: Prepare 3%Pt-CeO<sub>2</sub>-ZrO<sub>2</sub> (CeO<sub>2</sub>:ZrO<sub>2</sub> = 56:44, wt%) by coprecipitation, using nitrate precursors; % metal is by weight.MATERIALS  
(show actual weights used)

Pt nitrate solution, JM, 233.42 g Pt/l sol, 149.33 g Pt/kg sol. d = 1.5631 g/ml ..... 13.4 g  
 Ce(NO<sub>3</sub>)<sub>3</sub> stock solution, JM, 395 g Ce/l, d=1.7 g/ml ..... 120 g (~71 ml)  
 ZrO(NO<sub>3</sub>)<sub>2</sub> stock solution, JM, 203 g/l, d = 1.433 g/ml ..... 145 g (~101 ml)  
 NaOH pellets ..... 44.0 g  
 Deionized (DI) water (not including the water for washing the precipitate) ..... ~2000 ml

## Calculation

Calculated for 67 g 3%Pt-CeO<sub>2</sub>-ZrO<sub>2</sub> final material, containing:  
65 CeO<sub>2</sub>-ZrO<sub>2</sub> and 2 g Pt

- Pt nitrate solution needed for 2 g Pt:  
 $2 \times 1000 / 149.33 = 13.3932$  g Pt solution (8.568 ml)
- Ce (III) nitrate solution needed:  
 for 56% CeO<sub>2</sub>, 36.4 g CeO<sub>2</sub> in the final material  
 $\text{moles CeO}_2 = 36.4 / 172.12 = 0.21148 = \text{moles Ce}$   
 $\text{amount Ce} = 0.21148 \times 140.12 = 29.6326$  g  
 $\text{Ce(III) solution} = 29.6326 \times 1000 / 395 = 75.02$  ml Ce solution, or  $75.02 \times 1.7 = 127.533$  g Ce solution
- ZrO<sup>2+</sup> solution needed:  
 for 44% ZrO<sub>2</sub>, 28.6 g ZrO<sub>2</sub> in the final material  
 $\text{moles ZrO}_2 = 28.6 / 123.224 = 0.2321 = \text{moles Zr}$   
 $\text{amount Zr} = 0.2321 \times 91.224 = 21.1729$  g  
 $\text{ZrO}^{2+} \text{ solution} = 21.1729 \times 1000 / 203 = 104.3$  ml ZrO<sup>2+</sup> solution, or  $104.3 \times 1.433 = 149.462$  g ZrO<sup>2+</sup> solution
- NaOH solution needed, no excess:  
 $3 \text{ moles} / 1 \text{ mol Ce (III) solution}, 2 \text{ moles} / 1 \text{ mol ZrO}^{2+} \text{ solution}, 2 \text{ moles} / 1 \text{ mol Pt solution}$   
 $3 \times 0.21148 = 0.63444$  moles NaOH for Ce(III)  
 $2 \times 0.2321 = 0.4642$  moles NaOH for ZrO<sup>2+</sup>  
 $2 \times (2 / 195.09) = 0.020503$  moles NaOH for Pt  
 $\text{Total moles NaOH} = 1.11914$  moles;  
 $\text{NaOH needed: } 1.11914 \times 40 = 44.77$  g

## Preparation

The weighed amounts of Pt solution, Ce(III) solution, and zirconyl solution were mixed in an Erlenmeyer flask. The weighed amount of NaOH was brought to a 2-liter solution with DI water, in a volumetric flask (0.5N NaOH solution obtained), then transferred to the reactor.

The coprecipitation was conducted at 90-95°C in a 3-liter glass reactor having a heating/cooling mantle, under vigorous stirring, by dosing the Pt - Ce - Zr nitrate solution during ca. 1 hr, subsurface. The pump dial was set at "Other," display 0.5 in the beginning, then at 2.0, then the dosing accelerated to 3.0 pump dial. During the course of reaction, the color of the precipitate intensified from light yellow-beige to brown.

After the addition of the precursor solution was complete, the precipitate was cured under stirring for ca. 1 hr at 90°C, then let stand overnight. An additional 10 g solution NaOH (3 g pellets) was added before the stirring was stopped. The final pH was 8.

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Second day, the precipitate was washed and filtered repeatedly with a total of ~ 12 liter hot DI water (~55-60°C) to a filtrate pH 6. The washing step included slurring (redispersing) the precipitate into hot water (85-90°C) with stirring, followed by filtration. The conductivity of the filtrate was not measured.

After filtration, the material was placed in a crucible and dried overnight (~15 hr) at ~125°C in an oven, static air. The dried material (color dark brown) was calcined the second day in static air at 500°C for 2 hr. The catalyst was stored in a vial and labeled 1875-021 (1875-B). For WGS testing, the powder was pressed to 15 tons and sieved to 45-60 mesh.

**Observations**

The final pH (second day, June 29) was ~7, even though more NaOH had been added after the addition of Pt-Ce-Zr solutions.

**Results****Analytical**

| Pt % | Ce % | Ce(III)/Ce(IV) | Zr % | SA, m <sup>2</sup> /g | Pore Volume, cc/g | Pore Size Distribution | SEM | TEM | XRD | TPR/TPO | Pulse Chemisorption | ITK | Other |
|------|------|----------------|------|-----------------------|-------------------|------------------------|-----|-----|-----|---------|---------------------|-----|-------|
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A.G.

TITLE

PROJECT NO.

23

BOOK NO.

A.G.

File Name: 1875\_023 (4%Pt-CeO<sub>2</sub>-ZrO<sub>2</sub> 58-42 copp NaOH)

Tested as 1875-C

Catalyst prep: A. Ghenciu/ N. Trusry

## 5 Objective

WGS Catalyst: Prepare 4%Pt-CeO<sub>2</sub>-ZrO<sub>2</sub> (CeO<sub>2</sub>:ZrO<sub>2</sub> = 58:42, wt%) by coprecipitation, using nitrate precursors; % metal is by weight.

## MATERIALS

(shows actual weights used)

Pt nitrate solution, JM, 233.42 g Pt/l sol, 149.33 g Pt/kg sol, d = 1.5631 g/ml ..... 10.72 g  
Ce(NO<sub>3</sub>)<sub>3</sub> stock solution, JM, 395 g Ce/l, d = 1.7 g/ml ..... 78.95 g (~46.5 ml)  
ZrO(NO<sub>3</sub>)<sub>2</sub> stock solution, JM, 203 g/l, d = 1.433 g/ml ..... 84.28 g (~58.8 ml)  
NaOH pellets ..... 34.6 g  
Deionized (DI) water (not including the water for washing the precipitate) ..... ~2000 ml

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## Calculation

Calculated for 40 g 4%Pt-CeO<sub>2</sub>-ZrO<sub>2</sub> final material, containing:  
38.4 CeO<sub>2</sub>-ZrO<sub>2</sub> and 1.6 g Pt

1. Pt nitrate solution needed for 1.6 g Pt:

$$1.6 * 1000 / 149.33 = 10.715 \text{ g Pt solution (6.855 ml)}$$

2. Ce (III) nitrate solution needed:

for 58% CeO<sub>2</sub>, 22.272 g CeO<sub>2</sub> in the final material

$$\text{moles CeO}_2 = 22.272 / 172.12 = 0.129398 = \text{moles Ce}$$

$$\text{amount Ce} = 0.129398 * 140.12 = 18.1313 \text{ g}$$

$$\text{Ce(III) solution} = 18.1313 * 1000 / 395 = 45.90 \text{ ml Ce solution, or } 45.90 * 1.7 = 78.0333 \text{ g Ce solution}$$

3. ZrO<sup>2+</sup> solution needed:for 42% ZrO<sub>2</sub>, 16.128 g ZrO<sub>2</sub> in the final material

$$\text{moles ZrO}_2 = 16.128 / 123.224 = 0.130884 = \text{moles Zr}$$

$$\text{amount Zr} = 0.130884 * 91.224 = 11.9397 \text{ g}$$

$$\text{ZrO}^{2+} \text{ solution} = 11.9397 * 1000 / 203 = 58.8164 \text{ ml ZrO}^{2+} \text{ solution, or } 58.8164 * 1.433 = 84.2839 \text{ g ZrO}^{2+} \text{ solution}$$

4 NaOH solution needed, 30% excess:

3 moles/ 1 mol Ce (III) solution, 2 moles/ 1 mol ZrO<sup>2+</sup> solution, 2 moles/ 1 mol Pt solution

$$3 * 0.129398 = 0.388194 \text{ moles NaOH for Ce(III)}$$

$$2 * 0.130884 = 0.261767 \text{ moles NaOH for ZrO}^{2+}$$

$$2 * (1.6 / 195.09) = 0.016403 \text{ moles NaOH for Pt}$$

$$\text{Total moles NaOH} = 0.666364 \text{ moles; with 30\% excess, } 0.86627 \text{ moles NaOH}$$

$$\text{NaOH needed: } 0.86627 * 40 = 34.6509 \text{ g}$$

## Preparation

The weighed amounts of Pt solution, Ce(III) solution, and zirconyl solution were mixed in an Erlenmeyer flask. The weighed amount of NaOH was brought to a 2-liter solution with DI water, in a volumetric flask (0.43N NaOH solution obtained), then transferred to the reactor.

30 The coprecipitation was conducted at 90-95°C in a 3-liter glass reactor having a heating/cooling mantle, under vigorous stirring, by dosing the Pt - Ce - Zr nitrate solution during ca. 1 hr, subsurface. The pump dial was set at "Other," display 0.5-0.7 in the beginning, then at 2.0, then the dosing accelerated to 3.0 pump dial. During the course of reaction, the color of the precipitate intensified from light yellow to beige, then to brown.

After the addition of the precursor solution was complete, the precipitate was cured under stirring for ca. 1 hr at 90°C, then washed and filtered repeatedly with a total of ~14 liter hot DI water (~55-60°C) to a filtrate pH of 6. The washing step included slurring

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(redispersing) the precipitate into hot water (85-90°C) with stirring, followed by filtration. The conductivity of the filtrate was measured.

After filtration, the material was placed in a crucible and dried overnight (~15 hr) at ~125°C in an oven, static air. The dried material (color dark brown) was calcined the second day in static air at 500°C for 2 hr. The catalyst was stored in a vial and 1875-023 (1875-C). For WGS testing, the powder was pressed to 15 tons and sieved to 45-60 mesh.

**Observations**

Residue

Analysis

| Pt % | Ce % | Ce(III)/Ce(IV) | Zr % | SA, m <sup>2</sup> /g | Pore Volume, cc/g | Pore Size Distribution | SEM | TEM | XRD | TPR/TPO | Pulse Chemisorption | ITK | Other |
|------|------|----------------|------|-----------------------|-------------------|------------------------|-----|-----|-----|---------|---------------------|-----|-------|
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A.G.

TITLE

PROJECT NO.

25

BOOK NO.

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A. G.

File Name: 1875\_025 (ZrO2-4%Pt-CeO2 42-58 copp NaOH\_seq)

Tested as 1875-D

Catalyst prep: A. Ghenciu/ N. Trusty

## Objective

WGS Catalyst: Prepare ZrO2-4%Pt-CeO2 (CeO2:ZrO2 = 58:42, wt%) by sequential coprecipitation, using nitrate precursors; % metal is by weight. Target to obtain Pt-O-Ce(OH)x, then precipitate ZrO(OH)2.

## MATERIALS

(shows actual weights used)

Pt nitrate solution, JM, 233.42 g Pt/l sol, 149.33 g Pt/ kg sol, d = 1.5631 g/ml .....8.04 g  
 Ce(NO3)3 stock solution, JM, 395 g Ce/l, d=1.7 g/ml .....59.00 g (-34.7 ml)  
 ZrO(NO3)2 stock solution, JM, 203 g/l, d = 1.433 g/ml .....63.21 g (-44.1 ml)  
 NaOH pellets.....25.9 g  
 Deionized (DI) water (not including the water for washing the precipitate) .....-1500 ml

## Calculation

Calculated for 30 g 4%Pt-CeO2-ZrO2 final material, containing:

28.8 CeO2-ZrO2 and 1.2 g Pt

1. Pt nitrate solution needed for 1.2 g Pt:  
 $1.2 \times 1000 / 149.33 = 8.0359$  g Pt solution (5.141 ml)
2. Ce (III) nitrate solution needed:  
 for 58% CeO2, 16.704 g CeO2 in the final material  
 $\text{moles CeO}_2 = 16.704 / 172.12 = 0.09705 = \text{moles Ce}$   
 $\text{amount Ce} = 0.09705 \times 140.12 = 13.5984$  g  
 $\text{Ce(III) solution} = 13.5984 \times 1000 / 395 = 34.43$  ml Ce solution, or  $34.43 \times 1.7 = 58.525$  g Ce solution
3. ZrO<sup>2+</sup> solution needed:  
 for 42% ZrO2, 12.096 g ZrO2 in the final material  
 $\text{moles ZrO}_2 = 12.096 / 123.224 = 0.098163 = \text{moles Zr}$   
 $\text{amount Zr} = 0.098163 \times 91.224 = 8.95479$  g  
 $\text{ZrO}^{2+} \text{ solution} = 8.95479 \times 1000 / 203 = 44.1123$  ml ZrO<sup>2+</sup> solution, or  $44.1123 \times 1.433 = 63.213$  g ZrO<sup>2+</sup> solution
4. NaOH solution needed, 30% excess:  
 $3 \text{ moles / 1 mol Ce (III) solution, 2 moles / 1 mol ZrO}^{2+} \text{ solution, 2 moles / 1 mol Pt solution}$   
 $3 \times 0.09705 = 0.29115$  moles NaOH for Ce(III)  
 $2 \times 0.098163 = 0.196325$  moles NaOH for ZrO<sup>2+</sup>  
 $2 \times (1.2 / 195.09) = 0.012302$  moles NaOH for Pt  
 $\text{Total moles NaOH} = 0.49977$  moles; with 30% excess, 0.64971 moles NaOH  
 $\text{NaOH needed: } 0.64971 \times 40 = 25.9882$  g

## Preparation

The weighed amounts of Pt and Ce(III) solutions were stored in an Erlenmeyer flask. The weighed amount of zirconyl solution was stored in another Erlenmeyer flask. The necessary amount of NaOH was brought to 1.5-liter solution with DI water (0.43N NaOH solution obtained), then transferred to the reactor.

The coprecipitation was conducted at 90-95°C in a 1.5-liter glass reactor having a heating/cooling mantle, under vigorous stirring, in the following manner:

- The Pt - Ce nitrate solution was dosed in the NaOH solution during ca. 20 min, subsurface. The pump dial was set at "Other," display 0.5-0.7 in the beginning, then at 2.0 followed by 2.5 pump dial. During the course of the reaction, the color of the precipitate intensified from light yellow to dark beige.
- After the addition of the Pt-Ce solution was complete, the zirconyl solution was added by dosing in the same manner (pump dial 2.5, "Other"). The precipitate became slightly lighter in color, probably due to the formation of ZrO(OH)2.

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A. Ghenciu

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After the addition of the Zr precursor solution was complete, the precipitate was cured under stirring for ca. 1 hr at 90°C, then washed and filtered repeatedly with a total of ~ 11 liter hot DI water (~55-60°C) to a filtrate pH of 6. The washing step included slurring (redispersing) the precipitate in hot water (85-90°C) with stirring, followed by filtration. The conductivity of the filtrate was not measured.

The material was placed in a crucible and dried overnight (~15 hr) at -125°C in an oven, static air. The dried material (brown color) was calcined the second day in static air at 500°C for 2 hr. The catalyst was stored in a vial and labeled 1875-025 (1875-023). For WGS testing, the powder was pressed to 15 tons and sieved to 45-60 mesh.

Observations:

Compare the performance of 1875-023 and 1875-025 in WGS: Pt-CeO<sub>2</sub> or Pt-Ce-Zr interaction?

Physical Properties:

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| Pt % | Ce % | Ce(III)/Ce(IV) | Zr % | SA, m <sup>2</sup> /g | Pore Volume, cc/g | Pore Size Distribution | SEM | TEM | XRD | TPR/TPO | Pulse Chemisorption | ITK | Other |
|------|------|----------------|------|-----------------------|-------------------|------------------------|-----|-----|-----|---------|---------------------|-----|-------|
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PROJECT NO.

27

BOOK NO.

FILE

File Name: 1875\_027 (2%Pt-ZrO<sub>2</sub> copp NaOH)

Tested as 1875-E

Catalyst prep: A. Ghenciu/ N. Trusty

## Objective

WGS Catalyst: Prepare 2%Pt-ZrO<sub>2</sub> coprecipitation, using nitrate precursors; % metal is by weight. Target to obtain Pt-O-Zr(OH)<sub>x</sub>.

## MATERIALS

Actual  
Weight Used

Pt nitrate solution, 1M, 233.42 g Pt/l sol, 149.33 g Pt/kg sol, d = 1.5631 g/ml ..... 5.36 g  
ZrO(NO<sub>3</sub>)<sub>2</sub> stock solution, 1M, 203 g/l, d = 1.433 g/ml ..... 204.9 g (~143 ml)  
NaOH pellets ..... 30.9 g  
Deionized (DI) water (not including the water for washing the precipitate) ..... ~2000 ml

## Calculation

Calculated for 40 g 2%Pt-ZrO<sub>2</sub> final material, containing:  
39.2 ZrO<sub>2</sub> and 0.8 g Pt

1. Pt nitrate solution needed for 0.8 g Pt:  
 $0.8 \times 1000 / 149.33 = 5.3573$  g Pt solution (3.427 ml)

2. ZrO<sub>2</sub><sup>2+</sup> solution needed for 39.2 g ZrO<sub>2</sub> in the final material:  
moles ZrO<sub>2</sub> =  $39.2 / 123.224 = 0.31807$  = moles Zr  
amount Zr =  $0.31807 \times 91.224 = 29.0155$ g  
ZrO<sub>2</sub><sup>2+</sup> solution =  $29.0155 \times 1000 / 203 = 142.933$  ml ZrO<sub>2</sub><sup>2+</sup> solution, or  $142.933 \times 1.433 = 204.823$  g ZrO<sub>2</sub><sup>2+</sup> solution

3. NaOH solution needed, 20% excess:  
2 moles/ 1 mol ZrO<sub>2</sub><sup>2+</sup> solution, 2 moles/ 1 mol Pt solution  
 $2 \times 0.31807 = 0.63614$  moles NaOH for ZrO<sub>2</sub><sup>2+</sup>  
 $2 \times (0.8 / 195.09) = 0.008201$  moles NaOH for Pt  
Total moles NaOH = 0.64434 moles; with 20% excess, 0.7732 moles NaOH  
NaOH needed:  $0.7732 \times 40 = 30.93$  g

The weighed amounts of Pt and zirconyl solutions were stored in an Erlenmeyer flask. The necessary amount of NaOH was brought to 2-liter solution with DI water (0.38N NaOH solution obtained), then transferred to the reactor.

The coprecipitation was conducted at 90-95°C in a 3-liter glass reactor having a heating/cooling mantle, under vigorous stirring, by dosing the Pt - Zr nitrate solution during ca. ½ hr, subsurface. The pump dial was set at "Other," display 0.3-0.8 in the beginning, then at 2.0. During the course of reaction, the color of the precipitate intensified from light yellow to chrome yellow.

After the addition of the Pt-Zr precursor solution was complete, the precipitate was cured under stirring for ca. 1 hr at 90°C, then washed and filtered repeatedly with a total of ~ 12-13 liter hot DI water (~55-60°C) to a filtrate pH of 6. The washing step included slurring (redispersing) the precipitate in hot water (85-95°C) with stirring, followed by filtration. The conductivity of the filtrate was not measured.

After filtration, the material was placed in a crucible and dried overnight (~15 hr) at ~125°C in an oven, static air. The dried material was calcined the second day in static air at 500°C for 2 hr. The catalyst was stored in a vial and labeled 1875-027 (1875-E). For WGS testing, the powder was pressed to 15 tons and sieved to 45-60 mesh.

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A.G.

**Observations****Results &  
Analytical**

| Pt% | Zr% | SA,<br>m <sup>2</sup> /g | Pore<br>Volume,<br>cc/g | Pore Size<br>Distribution | SEM | TEM | XRD | TPR/<br>TPO | Pulse<br>Chemi-<br>sorption | ITK | Other |
|-----|-----|--------------------------|-------------------------|---------------------------|-----|-----|-----|-------------|-----------------------------|-----|-------|
|     |     |                          |                         |                           |     |     |     |             |                             |     |       |

## TITLE

PROJECT NO.

29

BOOK NO.

File Name: 1875\_029 (2%Pt-ZrO<sub>2</sub>-CeO<sub>2</sub> 42-58 copp NaOH\_seq)

Tested as 1875-F

Catalyst prep: A. Ghenciu, N. Trusty

## Objective

WGS Catalyst: Prepare 2%Pt-ZrO<sub>2</sub>-CeO<sub>2</sub> by coprecipitation, using nitrate precursors; % metal is by weight. Target to obtain Pt-O-Zr(OH)<sub>x</sub>-CeO<sub>x</sub>.MATERIALS  
(shows actual  
weights used)

Pt nitrate solution, JM, 233.42 g Pt/l sol, 149.33 g Pt/kg sol, d = 1.5631 g/ml ..... 2.68 g  
 Ce(NO<sub>3</sub>)<sub>3</sub> stock solution, JM, 395 g Ce/l, d=1.7 g/ml ..... 40.0 g (~23.5 ml)  
 ZrO(NO<sub>3</sub>)<sub>2</sub> stock solution, JM, 203 g/l, d = 1.433 g/ml ..... 43.0 g (~30 ml)  
 NaOH pellets ..... 16.1 g  
 Deionized (DI) water (not including the water for washing the precipitate) ..... ~1000 ml

## Calculation

Calculated for 20 g 2%Pt-ZrO<sub>2</sub>-CeO<sub>2</sub> final material, containing:  
19.6 CeO<sub>2</sub>-ZrO<sub>2</sub> and 0.4 g Pt

1. Pt nitrate solution needed for 0.4 g Pt:

$$0.4 * 1000 / 149.33 = 2.67863 \text{ g Pt solution (1 714 ml)}$$

2. Ce (III) nitrate solution needed:

for 58% CeO<sub>2</sub>, 11.368 g CeO<sub>2</sub> in the final material

$$\text{moles CeO}_2 = 11.368 / 172.12 = 0.066047 = \text{moles Ce}$$

$$\text{amount Ce} = 0.066047 * 140.12 = 9.2545 \text{ g}$$

$$\text{Ce(III) solution} = 9.2545 * 1000 / 395 = 23.43 \text{ ml Ce solution, or } 23.43 * 1.7 = 39.83 \text{ g Ce solution}$$

3. ZrO<sub>2</sub><sup>2+</sup> solution needed:for 42% ZrO<sub>2</sub>, 8.232 g ZrO<sub>2</sub> in the final material

$$\text{moles ZrO}_2 = 8.232 / 123.224 = 0.066805 \text{ moles Zr}$$

$$\text{amount Zr} = 0.066805 * 91.224 = 6.0942 \text{ g}$$

$$\text{ZrO}^{2+} \text{ solution} = 6.0942 * 1000 / 203 = 30.0209 \text{ ml ZrO}^{2+} \text{ solution, or } 30.0209 * 1.433 = 43.02 \text{ g ZrO}^{2+} \text{ solution}$$

4. NaOH solution needed, 20% excess:

3 moles/ 1 mol Ce (III) solution, 2 moles/ 1 mol ZrO<sub>2</sub><sup>2+</sup> solution, 2 moles/ 1 mol Pt solution

$$3 * 0.066047 = 0.198141 \text{ moles NaOH for Ce(III)}$$

$$2 * 0.066805 = 0.13361 \text{ moles NaOH for ZrO}^{2+}$$

$$2 * (0.4 / 195.09) = 0.0041 \text{ moles NaOH for Pt}$$

$$\text{Total moles NaOH} = 0.33585 \text{ moles; with 20\% excess, } 0.40302 \text{ moles NaOH}$$

$$\text{NaOH needed: } 0.40302 * 40 = 16.12 \text{ g}$$

## Preparation

The weighed amounts of Pt and zirconyl solutions were mixed and stored in an Erlenmeyer flask. The weighed amount of Ce(III) solution was stored in another Erlenmeyer flask. The necessary amount of NaOH was brought to 1-liter solution with DI water (0.4N NaOH solution obtained), then transferred to the reactor.

The coprecipitation was conducted at 90-95°C in a 1.5-liter glass reactor having a heating/cooling mantle, under vigorous stirring, in the following manner:

The Ce(III) nitrate solution was dosed in the NaOH solution during ca. 20 min. subsurface. The pump dial was set at "Other," display 0.5-0.7 in the beginning, then at 2.0 followed by 2.5 pump dial. During the course of the reaction, the color of the precipitate intensified from light pink-purple to a purple-cocoa color. After the addition of the Ce(III) solution was complete, the precipitate was cured for ¼ hr at 90-95°C under stirring.

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The Pt-Zr precursor solution was added by dosing in the same manner, subsurface, ca. 1/2 hr (pump dial 2.0-2.5, "Other"). precipitate turned yellowish-light brown.

The precipitate was cured under stirring for ca. 1 hr at 90°C, then washed and filtered repeatedly with a total of ~ 9-10 liter hot water (~55-60°C) to a filtrate pH of 6. The washing step included shurring (redispersing) the precipitate in hot water (85-95°C) with stirring, followed by filtration. The conductivity of the filtrate was not measured.

After filtration, the material was placed in a crucible and dried overnight (~15 hr) at ~125°C in an oven, static air. The dried material was calcined the second day in static air at 500°C for 2 hr. The catalyst was stored in a vial and labeled 1875-029 (1875-029 F). For WGS testing, the powder was pressed to 15 tons and sieved to 45-60 mesh.

Observations

Analysis

| Pt % | Ce % | Ce(III)/Ce(IV) | Zr % | SA, m <sup>2</sup> /g | Pore Volume, cc/g | Pore Size Distribution | SEM | TEM | XRD | TPR/TPO | Pulse Chemisorption | ITK | Other |
|------|------|----------------|------|-----------------------|-------------------|------------------------|-----|-----|-----|---------|---------------------|-----|-------|
|      |      |                |      |                       |                   |                        |     |     |     |         |                     |     |       |

*JP Review*

EXHIBIT "C"

**Smart, Evelyn**

**From:** Peter Gray [grayb.FCHO.READING@matthey.com]  
**Sent:**  
**To:** saller@gm.com  
**Cc:** oconnell@gm.com; piedmont@gm.com; robb@gm.com; stottler@gm.com;  
Wagner@gm.com; Mike Atkinson; Maeve Carney; Sue Ellis; Julia Evans; Jack Frost; Anca Ghenciu; Graham Hards; Mike Petch; Lu Potter; Jessica Reinkingh; Ros Stayne; Ian Wishart  
**Subject:** EXT: Records of Invention  
**Attachments:** RoI.zip



RoI.zip (1 MB)

Program: GM fuel processing sub program  
**Topic:** Records of Invention

Dear Jim,

Please find attached 19 RoIs for the items listed in your email of 26 July 2001. I have listed the concepts from your email in a summary document (RoI Status.doc), also attached.

Some concepts (7 and 14) have been covered as two RoIs, as they could possibly be regarded as two inventions.

Any concepts you have listed as "possible publication" I have also included as RoIs, just as a convenient way of documenting the ideas.

Would you address specific technical questions on any RoI to the appropriate author. Thanks. For any information on background IP, would you please contact Maeve. As per the MEA program, Maeve is putting together a package of previous JM patents which may be relevant background. She will send this to you next week.

We will be having our next monthly meeting in Honeoye Falls on September 18-19. I'm planning to schedule some time in the agenda to allow for further discussion of these RoIs. Do you have a preference for the Tuesday or Wednesday?

Best regards

Peter

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